

## Higher Random-Phase Approximation as an Approximation to the Equations of Motion

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Starting from the equations of motion expressed as ground-state expectation values, we have derived a higher-order random-phase approximation (RPA) for excitation frequencies of low-lying states. The matrix elements in the expectation value are obtained up to terms linear in the ground-state correlation coefficients. We represent the ground state as  $e^U|HF\rangle$ , where  $U$  is a linear combination of two particle-hole operators, and  $|HF\rangle$  is the Hartree-Fock ground state. We then retain terms only up to those linear in the correlation coefficients in the equation determining the ground state. This equation and that for the excitation energy are then solved self-consistently. We do not make the quasiboson approximation in this procedure, and explicitly discuss the overcounting characteristics of this approximation. The resulting equations have the same form as those of the RPA, but this higher RPA removes many deficiencies of the RPA.

## I. INTRODUCTION

The Hartree-Fock (HF) method has been successfully applied to various problems in atomic, molecular, nuclear, and solid-state physics. On the other hand, more precise methods are required to include the effects of electron correlation on various physical observables. This is particularly true in atomic and molecular physics. For instance, dissociation energies of molecules can be of the order of the correlation energy, and the ordering of atomic and molecular spectroscopic states can be considerably shifted by electron correlation. A straightforward way to improve the HF approximation is by configuration interaction (CI). An alternative and simpler approach is to use Sinanoğlu's<sup>1</sup> many-electron theory, which expands the correlation wave function in a series of pair correlation functions and their unlinked clusters, reducing the problem into sets of effective two-particle problems. These methods, however, must be applied separately to each stationary-state wave function. If one is interested in relative quantities such as excitation energies or oscillator strengths, such procedures are not optimal. The random-phase approximation (RPA) is one approach to calculating these relative quantities directly, treating the stationary-state wave functions as having secondary importance. The RPA has been successfully applied to the theory of the electron gas and in the interpretation of nuclear spectra. Because of the significant differences between such systems and the electronic structure of atoms and molecules, we cannot assume that the RPA will give a consistent interpretation of atomic and molecular spectra. Altick and Glassgold<sup>2</sup> used the RPA to predict excitation energies and oscillator strengths for various transitions in beryllium, magnesium, calcium, and strontium. We have used the RPA to study the

low-lying excited states of ethylene and formaldehyde to see how the approximation works for molecules. The results for transitions to singlet excited states were encouraging and the formalism of the RPA suggests some promising procedures for including the effects of electron correlation on the spectra of large conjugated molecules.<sup>3</sup> However, the RPA worked poorly for triplet excited states. Removal of this deficiency is one of the goals of this paper.

Various attempts have been made to improve and extend the RPA. The RPA violates the Pauli exclusion principle to some degree. In the equations-of-motion method of deriving the RPA this violation comes about because we approximate particle-hole pairs as bosons. There are other ways of deriving the RPA, e.g., the Green's-function method and the time-dependent HF theory. However, the equations-of-motion method is very flexible and, for example, has been used to derive a second RPA in which the excitation operator includes both two- and four-quasiparticle components.<sup>4</sup> The first attempt to consider ground-state correlation effects on the RPA was made by Ikeda, Udagawa, and Yamamura.<sup>5</sup> They took into account corrections to the one-body densities in the quasiboson approximation. Rowe<sup>6</sup> discussed other extensions of the RPA along with their limitations. Rowe<sup>6</sup> also proposed a new equation-of-motion method for studying excitation frequencies and oscillator strengths directly. The equations of motion are expressed as the ground-state expectation of operator equations. The formal equations become exact closed expressions which do not violate the exclusion principle and are not subject to the old objections to the RPA. The RPA is just the simplest approximation to the solution of these general equations. Rowe<sup>6</sup> derived a higher-order approximation to the solution of these equations in which the HF single-par-

particle energies and densities are replaced by renormalized quantities, e. g., the HF particle-hole energies are replaced by renormalized particle-hole energies. Rowe<sup>6</sup> suggested that the renormalized energies could be estimated from experiment and the single-particle densities calculated self-consistently. For applications to atomic and molecular systems this form of the theory is not very convenient. We show that the matrix elements in the equation determining the excitation frequency contain terms linear in the ground-state correlation coefficients. For applications to molecular spectra we would also like to calculate the ground-state correlations and the excitation frequency self-consistently.

In this paper we start from the equations-of-motion method proposed by Rowe<sup>6</sup> and obtain the various matrix elements up to terms linear in the ground-state correlation coefficients. We make no further assumptions in obtaining these equations. We then retain only up to linear terms in the cluster expansion in the equation determining the ground state. This equation and that for the excitation energy are then solved self-consistently. We do not make the quasiboson approximation in this procedure. In another paper<sup>7(a)</sup> we will apply these equations to study the excited states of ethylene for comparison with our previous RPA calculations on this system. We will discuss the types of practical approximations which can be used to simplify the problem considerably.

## II. ROWE'S EQUATIONS OF MOTION

Rowe<sup>6</sup> recently showed by equations of motion and by variational methods that the operator  $O_\lambda^\dagger$  for creating an excited state  $|\lambda\rangle$  from the ground state is a solution of the equation

$$\langle 0 | [\delta O_\lambda, H, O_\lambda^\dagger] | 0 \rangle = \omega_\lambda \langle 0 | [\delta O_\lambda, O_\lambda^\dagger] | 0 \rangle \quad (1)$$

for all variations  $\delta O_\lambda$  where

$$O_\lambda^\dagger | 0 \rangle = |\lambda\rangle, \quad (2a)$$

$$O_\lambda | 0 \rangle = 0. \quad (2b)$$

In Eq. (1),  $\omega_\lambda$  is the excitation energy  $E_\lambda - E_0$ , and the double commutator is defined by

$$2[A, B, C] = [A, [B, C]] + [[A, B], C]. \quad (3)$$

The solution of Eq. (1) gives the excitation energy of the state  $|\lambda\rangle$  relative to the correlated ground state  $|0\rangle$ . If one replaces the correlated ground state  $|0\rangle$  in Eq. (1) by the uncorrelated ground state, e. g., the HF function  $|\text{HF}\rangle$ , and restricts the excitation operator to single-particle-hole form, the solution of Eq. (1) is just the RPA. Our aim is to study the solutions of the equations of motion with correlated functions  $|0\rangle$  to see the effect of these correlations on the excitation energy. One of the advantages of Eq. (1) for including these effects is

that this expression contains the expectation value of a commutator and a double commutator. The commutator of two operators is of lower particle rank than the product of the two operators and its matrix elements are less sensitive to the complexities of the wave function  $|0\rangle$ . This is how the equations-of-motion method includes the effects of complexities in the wave functions on the excitation energy but bypasses the complexities themselves by calculating this relative quantity directly.

In the RPA, Eq. (1) is solved by assuming for  $|0\rangle$  the HF ground state. It is well known that this is a defect of the RPA since the HF wave function does not satisfy Eq. (2b), i. e.,

$$O_\lambda |\text{HF}\rangle \neq 0 \quad (4)$$

for the RPA excitation operator  $O_\lambda^\dagger$ . For the RPA,  $O_\lambda^\dagger$  is restricted to single-particle-hole operators

$$O^\dagger = \sum_{m'\gamma'} [Y_{m'\gamma'} C_{m'}^\dagger C_{\gamma'} - Z_{m'\gamma'} C_{\gamma'}^\dagger C_{m'}], \quad (5)$$

where  $\gamma'$  are hole states and  $m'$  are particle states. For atomic and molecular spectra Eq. (5) is a good approximation. However, from our earlier results on ethylene the approximation implied by Eq. (4) is a poor one for low-lying triplet states. To remedy this defect we need to know the correlated ground state  $|0\rangle$ . In this paper we develop a scheme for solving Eqs. (1) and (2b) self-consistently. We believe that the results will be useful in studying atomic and molecular spectra nonempirically and in developing semiempirical theories for their interpretation. We do not make the quasiboson approximation and, in fact, we will show elsewhere<sup>7</sup> that such an approximation works poorly for molecules. In this paper we present our formal results, but in Ref. 7(a) we will discuss various approximate methods for solving these equations.

Consider the excited state  $|\lambda \Gamma SM\rangle$ :

$$|\lambda \Gamma SM\rangle = O^\dagger(\lambda \Gamma SM) | 0 \rangle, \quad (6)$$

where  $SM$  specifies the spin state;  $\Gamma$  the irreducible representation of the molecular symmetry group; and  $\lambda$  the different eigenstates in the class  $(\Gamma SM)$ . We must solve Eq. (1) for excitation frequencies  $\omega_\lambda$  and Eq. (2b) for all states  $|\lambda\rangle$ :

$$O(\lambda \Gamma SM) | 0 \rangle = 0. \quad (7)$$

We also require orthogonality of excited-state wave functions,

$$\langle 0 | [O(\lambda' \Gamma' S' M'), O^\dagger(\lambda \Gamma SM)] | 0 \rangle = \delta_{\lambda'\lambda} \delta_{\Gamma'\Gamma} \delta_{S'S} \delta_{M'M}. \quad (8)$$

Note that we have assumed  $\langle 0 | 0 \rangle = 1$ . As in the RPA the operators  $O^\dagger(\lambda \Gamma SM)$  will contain only single-particle-hole operators:

$$O^\dagger(\lambda \Gamma SM) = \sum_{m\gamma(\Gamma)} [Y_{m\gamma}(\lambda S) C_{m\gamma}^\dagger(SM) - Z_{m\gamma}(\lambda S) C_{m\gamma}(\overline{SM})]. \quad (9)$$

For simplicity we will assume that the irreducible representation  $\Gamma$  to which the particle-hole pair  $m\gamma$  belongs is one dimensional. Extensions to general irreducible representations are straightforward. In Eq. (9),  $C_{m\gamma}^\dagger(SM)$  is a particle-hole creation operator defined as

$$C_{m\gamma}^\dagger(1M) = \begin{cases} -c_{m\alpha}^\dagger c_{\gamma\beta} & (M=1) \\ 2^{-1/2}[c_{m\alpha}^\dagger c_{\gamma\alpha} - c_{m\beta}^\dagger c_{\gamma\beta}] & (M=0) \\ c_{m\beta}^\dagger c_{\gamma\alpha} & (M=-1) \end{cases}$$

$$C_{m\gamma}^\dagger(00) = 2^{-1/2}[c_{m\alpha}^\dagger c_{\gamma\alpha} + c_{m\beta}^\dagger c_{\gamma\beta}], \quad (10)$$

$$C_{m\gamma}^\dagger(\overline{SM}) \equiv (-)^{S+M} C_{m\gamma}^\dagger(S-M). \quad (11)$$

Some useful properties of these operators are discussed in Appendix A. The index  $m$  refers to a particle-state orbital and  $\gamma$  to a hole. The subscripts  $\alpha$  and  $\beta$  denote the usual Pauli spinfunctions. For a closed-shell HF ground state we have  $c_{\gamma\alpha}^\dagger|\text{HF}\rangle = c_{m\alpha}|\text{HF}\rangle = 0$  and similarly for the operators  $c_{\gamma\beta}^\dagger$ ,  $c_{m\beta}$ . The particle-hole operators satisfy the equations (see Appendix A)

$$\begin{aligned} [S_\pm, C_{m\gamma}^\dagger(S, M)] &= [S(S+1) - M(M \pm 1)]^{1/2} C_{m\gamma}^\dagger(S, M \pm 1), \\ [S_z, C_{m\gamma}^\dagger(S, M)] &= M C_{m\gamma}^\dagger(S, M). \end{aligned} \quad (12)$$

It then follows that

$$\begin{aligned} [S_\pm, O^\dagger(\lambda\Gamma SM)] &= [S(S+1) - M(M \pm 1)]^{1/2} O^\dagger(\lambda\Gamma SM \pm 1), \\ [S_z, O^\dagger(\lambda\Gamma SM)] &= M O^\dagger(\lambda\Gamma SM). \end{aligned} \quad (13)$$

The summation in Eq. (9) extends over those pairs  $m\gamma$  which belong to the irreducible representation  $\Gamma$ .

Substitution of Eq. (9) for  $O^\dagger(\lambda\Gamma SM)$  into Eq. (1) gives the following equations for the amplitudes  $Y_{m\gamma}$  and  $Z_{m\gamma}$ :

$$\begin{aligned} \sum_{n\delta(\Gamma)} [\alpha_{m\gamma, n\delta}(S) Y_{n\delta}(\lambda S) + \beta_{m\gamma, n\delta}(S) Z_{n\delta}(\lambda S)] \\ = \omega(\lambda\Gamma S) \sum_{n\delta(\Gamma)} \mathcal{D}_{m\gamma, n\delta} Y_{n\delta}(\lambda S), \\ \sum_{n\delta(\Gamma)} [\alpha_{m\gamma, n\delta}^*(S) Z_{n\delta}(\lambda S) + \beta_{m\gamma, n\delta}^*(S) Y_{n\delta}(\lambda S)] \\ = -\omega(\lambda\Gamma S) \sum_{n\delta(\Gamma)} \mathcal{D}_{m\gamma, n\delta}^* Z_{n\delta}(\lambda S). \end{aligned} \quad (14)$$

( $m$  and  $n$  refer to particle states and  $\gamma$  and  $\delta$  to hole states) where

$$\begin{aligned} \alpha_{m\gamma, n\delta}(S) &\equiv \langle 0 | [C_{m\gamma}(SM), H, C_{n\delta}^\dagger(SM)] | 0 \rangle, \\ \beta_{m\gamma, n\delta}(S) &\equiv -\langle 0 | [C_{m\gamma}(SM), H, C_{n\delta}^\dagger(\overline{SM})] | 0 \rangle, \\ \mathcal{D}_{m\gamma, n\delta} &\equiv \langle 0 | [C_{m\gamma}(SM), C_{n\delta}^\dagger(SM)] | 0 \rangle. \end{aligned} \quad (15)$$

The matrix elements of  $\alpha$  and  $\beta$  do not depend on  $M$  and the matrix elements of  $\mathcal{D}$  do not depend on either  $S$  or  $M$ . (See Appendix B.) All these matrix elements vanish if  $m\gamma$  and  $n\delta$  belong to different irreducible representations. The equations can therefore be written for each  $\Gamma$  in matrix form

$$\begin{aligned} \begin{bmatrix} \underline{\alpha}^{(\Gamma)}(S) \underline{\beta}^{(\Gamma)}(S) \\ -\underline{\beta}^{(\Gamma)*}(S) - \underline{\alpha}^{(\Gamma)}(S) \end{bmatrix} \begin{bmatrix} Y^{(\Gamma)}(\lambda S) \\ Z^{(\Gamma)}(\lambda S) \end{bmatrix} = \omega(\lambda\Gamma S) \\ \times \begin{bmatrix} \underline{\mathcal{D}}^{(\Gamma)} & \underline{0} \\ \underline{0} & \underline{\mathcal{D}}^{(\Gamma)*} \end{bmatrix} \begin{bmatrix} Y^{(\Gamma)}(\lambda S) \\ Z^{(\Gamma)}(\lambda S) \end{bmatrix}. \end{aligned} \quad (14')$$

We write  $(\Gamma)$  on the submatrices to indicate the irreducibility of the equation.

Note that substitution of Eq. (9) into (8) gives

$$\begin{aligned} \sum_{m'\gamma'(\Gamma')} \sum_{m\gamma(\Gamma)} [Y_{m'\gamma'}^*(\lambda'S) \mathcal{D}_{m'\gamma', m\gamma} Y_{m\gamma}(\lambda S) \\ - Z_{m'\gamma'}^*(\lambda'S) \mathcal{D}_{m'\gamma', m\gamma}^* Z_{m\gamma}(\lambda S)] = \delta_{\lambda'\lambda} \delta_{\Gamma'\Gamma}. \end{aligned} \quad (16)$$

### III. HAMILTONIAN

In second-quantized form the Hamiltonian is<sup>3</sup>

$$\begin{aligned} H = \sum_i \epsilon_i c_i^\dagger c_i + \frac{1}{2} \sum_{i'j'k'l'} V_{i'j'k'l'} c_{j'}^\dagger c_{k'}^\dagger c_l c_{i'} \\ - \sum_{i'j' \gamma' \gamma} (V_{i'j' \gamma' \gamma} - V_{i' \gamma' j' \gamma}) c_{j'}^\dagger c_{\gamma'}^\dagger. \end{aligned} \quad (17)$$

The first term corresponds to the sum of HF single-particle Hamiltonians, the second to the Coulomb interactions, and the third to the HF potentials. The second and third terms are the residual interactions between electrons. In Eq. (17)  $\gamma'$  refers to a hole spin orbital and  $i', j', k', l'$  to any spin orbital, i.e., hole or particle. Unprimed indices refer to orbitals. The matrix elements of  $V$  are

$$V_{i'j'k'l'} = \langle i'(1)j'(2) | r_{12}^{-1} | k'(1)l'(2) \rangle. \quad (18)$$

Hence the matrix element of the HF potential  $v$  is

$$\langle i' | v | j' \rangle = \sum_{\gamma'} (V_{i' \gamma' j' \gamma'} - V_{i' \gamma' j' \gamma'}). \quad (19)$$

In terms of the multipole operators  $C_{ij}^\dagger(SM)$  (see Appendix A) the Hamiltonian can be written as

$$\begin{aligned} H = \sum_i \epsilon_i \sqrt{2} C_{ii}^\dagger(00) + \sum_{ij} [-\frac{1}{2} \sum_h V_{ikhj} \\ + \sum_{\gamma} (V_{i\gamma\gamma j} - 2V_{i\gamma j\gamma})] \sqrt{2} C_{ij}^\dagger(00) \\ + \sum_{ijkl} V_{ijkl} C_{ik}^\dagger(00) C_{jl}^\dagger(00). \end{aligned} \quad (20)$$

### IV. GROUND STATE

The true ground state of the system can be written:

$$|0\rangle = N_0[|\text{HF}\rangle + |\chi\rangle]; \quad \langle\chi|\text{HF}\rangle = 0, \quad (21)$$

where  $|\text{HF}\rangle$  is the HF wave function and  $|\chi\rangle$  the correlation wave function for the ground state. Clearly, for the systems of electrons in atoms and molecules we have

$$\langle\chi|\chi\rangle/\langle\text{HF}|\text{HF}\rangle \ll 1. \quad (22)$$

Sinanoğlu<sup>1</sup> showed that  $|\chi\rangle$  is well approximated for closed-shell systems of atoms and molecules by including the pair correlation functions and their

unlinked clusters. The wave function of Eq. (21) can then be written<sup>8</sup>

$$|0\rangle \approx N_0 e^U |HF\rangle; \quad e^U = 1 + U + \frac{1}{2}U^2 + \dots, \quad (23)$$

where

$$U = \sum_{\gamma' < \delta'} \hat{u}_{\gamma'\delta'}^\dagger c_{\delta'} c_{\gamma'}. \quad (24)$$

The  $\hat{u}$ 's have the following properties:

$$\begin{aligned} (\hat{u}_{\gamma'\delta'}^\dagger)^\dagger |HF\rangle &= 0, \quad [\hat{u}_{\gamma'\delta'}^\dagger, \hat{u}_{\mu'\nu'}^\dagger] = 0; \\ [c_{\gamma'}, \hat{u}_{\mu'\nu'}^\dagger] &= [c_{\gamma'}^\dagger, \hat{u}_{\mu'\nu'}^\dagger] = 0. \end{aligned} \quad (25)$$

In CI notation we have

$$\hat{u}_{\gamma'\delta'}^\dagger = \sum_{m' < n'} C_{\gamma'\delta'}^{m'n'} c_{m'}^\dagger c_{n'}^\dagger. \quad (26)$$

Note that all Greek letters refer to hole states and the Latin letters  $m, n$  to particle states. Wave functions of the form of Eq. (23) have also been used in discussing applications of the RPA to nuclear physics.<sup>9-11</sup>

Instead of using the coefficients  $C_{\gamma'\delta'}^{m'n'}$ , we write

$$U = \sum_{mn \gamma\delta} \{K_{m\gamma, n\delta} c_{m\alpha}^\dagger c_{n\beta}^\dagger c_{\delta\beta} c_{\gamma\alpha} + \frac{1}{2} L_{m\gamma, n\delta} [c_{m\alpha}^\dagger c_{n\alpha}^\dagger c_{\delta\alpha} c_{\gamma\alpha} + c_{m\beta}^\dagger c_{n\beta}^\dagger c_{\delta\beta} c_{\gamma\beta}]\}. \quad (27)$$

Note that we are considering only closed-shell ground-state HF functions in Eq. (23). The matrices of coefficients  $K$  and  $L$  are symmetric:

$$K_{m\gamma, n\delta} = K_{n\delta, m\gamma}, \quad L_{m\gamma, n\delta} = L_{n\delta, m\gamma}. \quad (28)$$

Also  $U$  is unchanged if  $L_{m\gamma, n\delta}$  is replaced by  $\frac{1}{2}(L_{m\gamma, n\delta} - L_{m\delta, n\gamma})$ . The coefficients of Eq. (26) are related to those of Eq. (27) by

$$\begin{aligned} C_{\gamma\alpha\delta\beta}^{m\alpha n\beta} &= C_{\gamma\beta\delta\alpha}^{m\beta n\alpha} = K_{m\gamma, n\delta}, \quad C_{\gamma\alpha\delta\beta}^{m\beta n\alpha} = C_{\gamma\beta\delta\alpha}^{m\alpha n\beta} = -K_{m\delta, n\gamma}, \\ C_{\gamma\alpha\delta\alpha}^{m\alpha n\beta} &= C_{\gamma\beta\delta\beta}^{m\beta n\alpha} = L_{m\gamma, n\delta} - L_{m\delta, n\gamma}. \end{aligned} \quad (29)$$

For simplicity we are assuming that all irreducible representations of the molecular symmetry are one dimensional. The coefficients  $K$  and  $L$  must vanish if the particle-hole pairs  $m\gamma$  and  $n\delta$  belong to different irreducible representations, and, hence, the matrices  $K$  and  $L$  with elements  $K_{m\gamma, n\delta}$  and  $L_{m\gamma, n\delta}$  are block diagonal.

Note that

$$\begin{aligned} C_{m\gamma}^\dagger(00) C_{n\delta}^\dagger(00) + C_{m\gamma}^\dagger(10) C_{n\delta}^\dagger(\overline{10}) \\ = c_{m\alpha}^\dagger c_{n\beta}^\dagger c_{\delta\beta} c_{\gamma\alpha} + c_{n\alpha}^\dagger c_{m\beta}^\dagger c_{\gamma\beta} c_{\delta\alpha}, \end{aligned} \quad (30a)$$

$$\begin{aligned} C_{m\gamma}^\dagger(00) C_{n\delta}^\dagger(00) - C_{m\gamma}^\dagger(00) C_{n\delta}^\dagger(\overline{10}) \\ = c_{m\alpha}^\dagger c_{n\alpha}^\dagger c_{\delta\alpha} c_{\gamma\alpha} + c_{m\beta}^\dagger c_{n\beta}^\dagger c_{\delta\beta} c_{\gamma\beta}. \end{aligned} \quad (30b)$$

Then Eq. (27) can be written:

$$\begin{aligned} U = \frac{1}{2} \sum_{mn \gamma\delta} [K_{m\gamma, n\delta} \sum_{S=0,1} C_{m\gamma}^\dagger(S0) C_{n\delta}^\dagger(\overline{S0}) \\ + \frac{1}{2} (L_{m\gamma, n\delta} - L_{m\delta, n\gamma}) \sum_{S=0,1} (-1)^S C_{m\gamma}^\dagger(S0) C_{n\delta}^\dagger(\overline{S0})] \end{aligned} \quad (31)$$

or

$$U = \frac{1}{2} \sum_{mn \gamma\delta} \sum_S C_{m\gamma, n\delta}'(S) C_{m\gamma}^\dagger(S0) C_{n\delta}^\dagger(\overline{S0}), \quad (32)$$

where

$$C_{m\gamma, n\delta}'(S) = K_{m\gamma, n\delta} + (-1)^{\frac{S-1}{2}} (L_{m\gamma, n\delta} - L_{m\delta, n\gamma}). \quad (33)$$

The following form for  $U$  has been used in applications to nuclear spectroscopy<sup>9-11</sup>:

$$U = \frac{1}{2} \sum_{mn, \gamma\delta} \sum_{SM} C_{m\gamma, n\delta}''(S) C_{m\gamma}^\dagger(SM) C_{n\delta}^\dagger(\overline{SM}). \quad (34)$$

This is not an appropriate form for our purpose since we do not plan to use the quasiboson approximation. In fact it is easy to see that the four operators  $C_{m\gamma}^\dagger(SM) C_{n\delta}^\dagger(\overline{SM})$  for  $S=0, 1$  in Eq. (34) are not linearly independent. The assumption that these coefficients are linearly independent leads to the overcounting characteristic of the quasiboson approximation. This is discussed in Appendix D.

The usual way to determine  $U$  is to solve the variational equation directly. In Sinanoğlu's many-electron theory this equation is reduced by a perturbation-variation method to a set of pair equations for  $\hat{u}$ 's which are directly soluble. The coefficients in Eq. (26) can be determined in a straightforward manner. In the CI method  $U$  of Eq. (27) may be used truncating the sum over particle states. The equations can then be solved variationally for the  $K$  and  $L$  coefficients.

We will, however, determine  $U$  in quite a different manner. We attempt to obtain  $U$  by solving Eq. (7) and Eq. (14), which determines the excitation energy, self-consistently. To set up an iterative scheme we take the  $U$  of Eq. (27), express the matrix elements of  $\alpha$ ,  $\beta$ , and  $\mathfrak{D}$  in terms of the coefficients  $K$  and  $L$ , and solve Eq. (27) subject to the constraints on the correlation coefficients and the amplitudes  $Y$  and  $Z$  expressed in Eq. (7).

#### V. EQUATION $O(\lambda \Gamma SM)|0\rangle=0$

To determine the correlated ground state and the excitation energies and the associated amplitudes, we must solve Eqs. (7) and (15) self-consistently. In this section we deal with Eq. (7).

With  $|0\rangle$  of Eq. (23) and Eq. (9) for  $O^\dagger(\lambda \Gamma SM)$ , we have

$$O(\lambda \Gamma SM) (1 + U + \frac{1}{2}U^2 + (3!)^{-1}U^3 + \dots) |HF\rangle = 0. \quad (35)$$

Also we have

$$O(\lambda \Gamma SM) |HF\rangle = - \sum_{m\gamma(\Gamma)} Z_{m\gamma}^* (\lambda S) C_{m\gamma}^\dagger(\overline{SM}) |HF\rangle. \quad (36)$$

As is shown in Appendix C, we can write

$$C_{m\gamma}(SM) U |HF\rangle = \sum_{n\delta} C_{m\gamma, n\delta}(S) C_{n\delta}^\dagger(\overline{SM}) |HF\rangle, \quad (37)$$

where

$$C_{m\gamma, n\delta}(S) = K_{m\gamma, n\delta} + (-1)^S (K_{m\gamma, n\delta} - K_{m\delta, n\gamma}), \quad (38)$$

$$K_{m\gamma, n\delta} - K_{m\delta, n\gamma} = L_{m\gamma, n\delta} - L_{m\delta, n\gamma}. \quad (39)$$

Now  $C_{m\gamma}^*(\overline{SM})U|HF\rangle$  is a three-particle-hole term and is coupled to  $C_{m\gamma}(\overline{SM})U^2|HF\rangle$ , and so forth. Equation (35) becomes

$$\left\{ \left[ - \sum_{m\gamma(\Gamma)} Z_{m\gamma}^*(\lambda S) C_{m\gamma}^*(\overline{SM}) + \sum_{m\gamma(\Gamma)} Y_{m\gamma}^*(\lambda S) \right. \right. \\ \left. \left. \times \sum_{n\delta} C_{m\gamma, n\delta}(S) C_{n\delta}^*(\overline{SM}) \right] + \dots \right\} |HF\rangle = 0. \quad (40)$$

The terms not explicitly shown contain three-, five-, etc., particle-hole creation operators.

Equation (40) can be solved by equating to 0 the coefficients of all the linearly independent components on the left-hand side of the equation. For the single-particle-hole components we have ( $m\gamma \in \Gamma$ )

$$Z_{m\gamma}^*(\lambda S) = \sum_{n\delta(\Gamma)} Y_{n\delta}^*(\lambda S) C_{n\delta, m\gamma}(S) \quad (41)$$

and

$$C_{m\gamma, n\delta}(S) = 0 \quad \text{if } n\delta \notin \Gamma. \quad (42)$$

Equation (42) follows from the fact that the matrices of correlation coefficients  $K$ 's and  $L$ 's are block diagonal and their irreducible submatrices are characterized by  $\Gamma$ . The matrix of coefficients  $\underline{C}$  is symmetric since the matrices  $\underline{K}$  and  $\underline{L}$  are symmetric:

$$C_{m\gamma, n\delta}(S) = C_{n\delta, m\gamma}(S), \\ C_{m\gamma, n\gamma}(0) = C_{m\gamma, n\gamma}(1); \quad C_{m\gamma, m\delta}(0) = C_{m\gamma, m\delta}(1). \quad (43)$$

We can now rewrite Eq. (41):

$$Z_{m\gamma}^*(\lambda S) = \sum_{n\delta(\Gamma)} C_{m\gamma, n\delta}(S) Y_{n\delta}^*(\lambda S) \quad (44)$$

or, in matrix form,

$$\underline{Z}^{*(\Gamma)}(S) = \underline{C}^{(\Gamma)}(S) \underline{Y}^{*(\Gamma)}(\lambda S). \quad (45)$$

The coefficients of the components containing three-particle-hole operators can be treated similarly. These coefficients are, however, one order higher in the correlation coefficients and are certainly less important than those we included above. Including these terms would be inconsistent with restricting the excitation operator  $O_\lambda^\dagger$  to contain only single-particle-hole operators [Eq. (9)]. To include such terms we would have to go over to a second-RPA type of formulation.<sup>5</sup> For most problems of interest, Eq. (45) should be a very good approximation. Equation (45) has the same form as the equation derived by solving Eq. (7) with the  $U$  of Eq. (34) and the quasiboson approximation. Methods for solving this type of equation have been discussed by Sanderson and da Providência.<sup>10</sup> However, see Appendix D for the overcounting problem in the quasiboson approximation.)

#### VI. MATRIX ELEMENTS OF $\mathcal{Q}$ AND $\mathcal{B}$

We now derive explicit expressions for the matrix elements of  $\mathcal{Q}(S)$  and  $\mathcal{B}(S)$  as a function of the correlation coefficients. We have

$$\mathcal{Q}_{m\gamma, n\delta}(S) = N_0^2 A_{m\gamma, n\delta}(S), \quad \mathcal{B}_{m\gamma, n\delta}(S) = N_0^2 B_{m\gamma, n\delta}(S), \quad (46)$$

where

$$A_{m\gamma, n\delta}(S) \equiv \langle HF | e^{U\dagger} [C_{m\gamma}(SM), H, C_{n\delta}^\dagger(SM)] e^U | HF \rangle, \\ B_{m\gamma, n\delta}(S) \equiv - \langle HF | e^{U\dagger} [C_{m\gamma}(SM), H, C_{n\delta}^\dagger(\overline{SM})] e^U | HF \rangle. \quad (47)$$

We expand Eqs. (47) in a power series in  $U$ :

$$\underline{A}(S) = \underline{A}^{(0)}(S) + \underline{A}^{(1)}(S) + \dots, \\ \underline{B}(S) = \underline{B}^{(0)}(S) + \underline{B}^{(1)}(S) + \dots. \quad (48)$$

For convenience we write the Hamiltonian as a sum of three parts:

$$H = H(1) + H(2) + H(3); \quad H(1) \equiv \sum_i \epsilon_i \sqrt{2} C_{ii}^\dagger(00), \\ H(2) \equiv \sum_{ij} \left[ -\frac{1}{2} \sum_k V_{ik, kj} + \sum_\gamma (V_{i\gamma, \gamma j} - 2V_{i\gamma, j\gamma}) \right] \\ \times \sqrt{2} C_{ij}^\dagger(00), \quad (49)$$

$$H(3) = \sum_{ijkl} V_{ijkl} C_{ik}^\dagger(00) C_{jl}^\dagger(00).$$

With the properties of the operators  $C_{ij}^\dagger(SM)$  (Appendix A) we can obtain expressions for the matrix elements [Eq. (48)] to arbitrary order. Here we shall derive only the zero- and first-order terms in detail. We can make no basic improvement by including the higher-order terms, e.g.,  $A^{(2)}$  in Eq. (48) if the excited-state operator contains only single-particle-hole operators.

#### A. Matrix Elements of $A(S)$

We have

$$A_{m\gamma, n\delta}^{(0)}(S) \equiv \langle HF | [C_{m\gamma}(SM), H, C_{n\delta}^\dagger(SM)] | HF \rangle \\ = \langle HF | C_{m\gamma}(SM) H C_{n\delta}^\dagger(SM) | HF \rangle \\ - \delta_{mn} \delta_{\gamma\delta} \langle HF | H | HF \rangle, \quad (50)$$

$$\langle HF | H | HF \rangle = 2 \sum_\gamma \epsilon_\gamma - \sum_{\gamma\delta} (2J_{\gamma\delta} - K_{\gamma\delta}), \quad (51)$$

$$\langle HF | C_{m\gamma}(SM) H(1) C_{n\delta}^\dagger(SM) | HF \rangle = \delta_{mn} \delta_{\gamma\delta} \left[ \sum_n 2\epsilon_n + (\epsilon_m - \epsilon_\gamma) \right],$$

$$\langle HF | C_{m\gamma}(SM) H(2) C_{n\delta}^\dagger(SM) | HF \rangle \\ = - \delta_{mn} \delta_{\gamma\delta} \sum_\mu \left[ \sum_k K_{\mu k} + 2 \sum_\eta (2J_{\mu\eta} - K_{\mu\eta}) \right] \\ - \delta_{\gamma\delta} \left[ \frac{1}{2} \sum_k V_{mkkn} + \sum_\eta (2V_{\nu m\eta n} - V_{\nu mn\eta}) \right] \\ + \delta_{mn} \left[ \frac{1}{2} \sum_k V_{\delta k k \gamma} + \sum_\nu (2V_{\nu \delta \nu \gamma} - V_{\nu \delta \gamma \nu}) \right], \quad (52)$$

$$\langle HF | C_{m\gamma}(SM) H(3) C_{n\delta}^\dagger(SM) | HF \rangle \\ = \delta_{SM, 00} 2V_{m\delta\gamma n} - V_{m\delta n\gamma} + \delta_{mn} \delta_{\gamma\delta} \left( 2 \sum_{\mu\nu} J_{\mu\nu} \right. \\ \left. + \sum_{p\nu} K_{\nu p} \right) + \delta_{\gamma\delta} \left[ \sum_\mu (2V_{m\mu n\mu} - \frac{1}{2} V_{m\mu\mu n}) + \frac{1}{2} \sum_p V_{m\delta p n} \right] \\ + \delta_{mn} \left[ \sum_\mu (-2V_{\delta\mu\gamma\mu} + \frac{1}{2} V_{\delta\mu\mu\gamma}) - \frac{1}{2} \sum_p V_{\delta p p \gamma} \right],$$

$$\langle HF | C_{m\gamma}(SM) H C_{n\delta}^\dagger(SM) | HF \rangle$$

$$= \delta_{mn} \delta_{\gamma\delta} [\langle \text{HF} | H | \text{HF} \rangle + (\epsilon_m - \epsilon_\gamma)] \\ + \delta_{SM,00} 2V_{m\delta\gamma n} - V_{m\delta n\gamma}.$$

Thus, we have

$$A_{m\gamma, n\delta}^{(0)}(S) = \delta_{mn} \delta_{\gamma\delta} (\epsilon_m - \epsilon_\gamma) + [1 + (-1)^S] V_{m\delta\gamma n} - V_{m\delta n\gamma}. \quad (53)$$

This is the matrix element used in the Tamm-Dancoff approximation and in the usual RPA.

We now obtain the first-order term  $A_{m\gamma, n\delta}^{(1)}(S)$ :

$$A_{m\gamma, n\delta}^{(1)}(S) \equiv \langle \text{HF} | U^\dagger [C_{m\gamma}(SM), H, C_{n\delta}^\dagger(SM)] | \text{HF} \rangle \\ + \langle \text{HF} | [C_{m\gamma}(SM), H, C_{n\delta}^\dagger(SM)] U | \text{HF} \rangle \\ = \langle \text{HF} | U^\dagger [C_{m\gamma}(SM), H(3), C_{n\delta}^\dagger(SM)] | \text{HF} \rangle \\ + \langle \text{HF} | [C_{m\gamma}(SM), H(3), C_{n\delta}^\dagger(SM)] U | \text{HF} \rangle. \quad (54)$$

Evaluating Eq. (54), we have

$$\langle \text{HF} | U^\dagger [C_{m\gamma}(SM), H(3), C_{n\delta}^\dagger(SM)] | \text{HF} \rangle \\ = -\frac{1}{2} [\delta_{\gamma\delta} \sum_{q\mu\nu} V_{mq\mu\nu} \langle \text{HF} | U^\dagger C_{n\delta}^\dagger(00) C_{q\nu}^\dagger(00) | \text{HF} \rangle \\ + \delta_{mn} \sum_{pq\nu} V_{pq\gamma\nu} \langle \text{HF} | U^\dagger C_{p\delta}^\dagger(00) C_{q\nu}^\dagger(00) | \text{HF} \rangle], \quad (55a)$$

$$\langle \text{HF} | [C_{m\gamma}(SM), H(3), C_{n\delta}^\dagger(SM)] U | \text{HF} \rangle \\ = -\frac{1}{2} [\delta_{\gamma\delta} \sum_{q\mu\nu} V_{\mu\nu nq} \langle \text{HF} | C_{m\mu}(00) C_{q\nu}(00) U | \text{HF} \rangle \\ + \delta_{mn} \sum_{pq\nu} V_{\delta\nu pq} \langle \text{HF} | C_{p\gamma}(00) C_{q\nu}(00) U | \text{HF} \rangle]. \quad (55b)$$

The zero-order term  $B_{m\gamma, n\delta}^{(0)}(S)$  is

$$B_{m\gamma, n\delta}^{(0)}(S) = \langle \text{HF} | C_{m\gamma}(S, M) C_{n\delta}(\overline{SM}) H(3) | \text{HF} \rangle = \sum_{pq\mu\nu} V_{pq\mu\nu} \langle \text{HF} | C_{m\gamma}(SM) C_{n\delta}(\overline{SM}) C_{p\mu}^\dagger(00) C_{q\nu}^\dagger(00) | \text{HF} \rangle \\ = [1 + (-1)^S] V_{mn\gamma\delta} - (-1)^S V_{mn\delta\gamma} = \begin{cases} 2V_{mn\gamma\delta} - V_{mn\delta\gamma}, & (S=0) \\ V_{mn\delta\gamma}, & (S=1). \end{cases} \quad (60)$$

This is the matrix element used in the RPA. The first term in  $B_{m\gamma, n\delta}^{(1)}(S)$  [Eq. (59b)] vanishes because  $U^\dagger$  contains two-particle-hole annihilation operators and  $H(3)$  contains at best two-particle-hole creation operators still leaving a total of two-particle-hole operators in the matrix element:

$$B_{m\gamma, n\delta}^{(1)}(S) = -\langle \text{HF} | [C_{m\gamma}(SM), H(3), C_{n\delta}(\overline{SM})] U | \text{HF} \rangle$$

Equation (61) becomes

$$B_{m\gamma, n\delta}^{(1)}(S) = -\sqrt{2} \sum_{ijkl} V_{ijkl} \langle \text{HF} | \{C_{m\gamma}(SM), C_{ik}^\dagger(00) [\delta_{i\delta} C_{nj}(\overline{SM}) - \delta_{jn} C_{i\delta}(\overline{SM})]\} U | \text{HF} \rangle \\ = -(-1)^S \sum_{ik} \langle \text{HF} | C_{ki}(00) [V_{imk\delta} C_{n\gamma}(00) + V_{ink\gamma} C_{m\delta}(00)] U | \text{HF} \rangle \\ - \sum_{ijkl} V_{ijkl} \langle \text{HF} | [\delta_{im} C_{k\gamma}(SM) - \delta_{k\gamma} C_{mi}(SM)] [\delta_{i\delta} C_{nj}(\overline{SM}) - \delta_{jn} C_{i\delta}(\overline{SM})] U | \text{HF} \rangle, \quad (63)$$

and thus

$$B_{m\gamma, n\delta}^{(1)}(S) = -(-1)^S \sum_{p\mu} [V_{m\mu\delta} C_{p\mu, n\gamma}(0) + V_{n\mu\gamma\delta} C_{p\mu, m\delta}(0)]$$

With the results of Eqs. (C10)–(C13) of Appendix C we can write

$$A_{m\gamma, n\delta}^{(1)}(S) = -\delta_{\gamma\delta} \sum_{q\mu\nu} \frac{1}{2} [V_{mq\mu\nu} C_{n\mu, q\nu}^*(0) + V_{\mu\nu nq} C_{m\mu, q\nu}(0)] \\ - \delta_{mn} \sum_{pq\nu} \frac{1}{2} [V_{pq, \gamma\nu} C_{p\delta, q\nu}^*(0) + V_{\delta\nu pq} C_{p\gamma, q\nu}(0)], \quad (56)$$

which is independent of  $S$ .

#### B. Matrix Elements of $B(S)$

First note that

$$[C_{m\gamma}(SM), C_{ij}^\dagger(00), C_{n\delta}(\overline{SM})] = 0, \quad (57a)$$

if  $i$  and  $j$  are both particle states or both hole states. However, we also have

$$\langle 0 | [C_{m\gamma}(SM), C_{ij}^\dagger(00), C_{n\delta}(\overline{SM})] | 0 \rangle = 0, \quad (57b)$$

if one of the states  $i$  and  $j$  is a hole state and the other a particle state. Hence we have

$$B_{m\gamma, n\delta}(S) = -\langle \text{HF} | e^{U^\dagger} [C_{m\gamma}(SM), H(3), C_{n\delta}(\overline{SM})] e^U | \text{HF} \rangle, \quad (58)$$

$$B_{m\gamma, n\delta}^{(0)}(S) = -\langle \text{HF} | [C_{m\gamma}(SM), H(3), C_{n\delta}(\overline{SM})] | \text{HF} \rangle, \quad (59a)$$

$$B_{m\gamma, n\delta}^{(1)}(S) = -\{\langle \text{HF} | U^\dagger [C_{m\gamma}(SM), H(3), C_{n\delta}(\overline{SM})] | \text{HF} \rangle \\ + \langle \text{HF} | [C_{m\gamma}(SM), H(3), C_{n\delta}(\overline{SM})] U | \text{HF} \rangle\}. \quad (59b)$$

$$= -\langle \text{HF} | [C_{m\gamma}(SM), [H(3), C_{n\delta}(SM)]] U | \text{HF} \rangle. \quad (61)$$

Also, we have

$$[C_{ik}^\dagger(00) C_{ji}^\dagger(00), C_{n\delta}(\overline{SM})] = 2^{-1/2} \{C_{ik}^\dagger(00) [\delta_{i\delta} C_{nj}(\overline{SM}) \\ - \delta_{jn} C_{i\delta}(SM)] + C_{ji}^\dagger(00) [\delta_{n\delta} C_{ni}(\overline{SM}) \\ - \delta_{in} C_{k\delta}(\overline{SM})]\} + \frac{1}{2} \{\delta_{n\delta} [\delta_{jn} C_{ii}(\overline{SM}) - \delta_{ii} C_{nj}(\overline{SM})] \\ - \delta_{in} [\delta_{jk} C_{i\delta}(\overline{SM}) - \delta_{i\delta} C_{kj}(\overline{SM})]\}. \quad (62)$$

$$- \sum_{p\mu} [V_{m\mu\delta} C_{p\gamma, n\mu}(S) + V_{n\mu\delta\gamma} C_{m\mu, p\delta}(S)] \\ + \sum_{pq} V_{mn\delta p} C_{p\gamma, q\delta}(S) + \sum_{\mu\nu} V_{\mu\nu\gamma\delta} C_{m\mu, n\nu}(S). \quad (64)$$

### VII. MATRIX ELEMENTS OF $\mathcal{D}$ AND ONE-ELECTRON DENSITIES

From Eq. (B3) in Appendix B, we have

$$\mathcal{D}_{m\gamma, n\delta} = \delta_{mn} \rho_{\gamma\delta} - \delta_{\gamma\delta} \rho_{nm}, \quad (65a)$$

where

$$\rho_{ij} = \langle 0 | c_{i\alpha}^\dagger c_{j\alpha} | 0 \rangle. \quad (65b)$$

Defining

$$p_{ij} = \langle \text{HF} | e^{U^\dagger} c_{i\alpha}^\dagger c_{j\alpha} e^U | \text{HF} \rangle, \quad (66a)$$

$$D_{m\gamma, n\delta} \equiv \delta_{mn} p_{\gamma\delta} - \delta_{\gamma\delta} p_{nm}, \quad (66b)$$

we have

$$\mathcal{D}_{m\gamma, n\delta} = N_0^2 D_{m\gamma, n\delta}; \quad \rho_{ij} = N_0^2 p_{ij}. \quad (67)$$

Expanding Eq. (66a), we have

$$p_{ij} = p_{ij}^{(0)} + p_{ij}^{(1)} + p_{ij}^{(2)} + \dots, \quad (68a)$$

where

$$\begin{aligned} p_{ij}^{(0)} &= \langle \text{HF} | c_{i\alpha}^\dagger c_{j\alpha} | \text{HF} \rangle, \\ p_{ij}^{(1)} &= \langle \text{HF} | U^\dagger c_{i\alpha}^\dagger c_{j\alpha} + c_{i\alpha}^\dagger c_{j\alpha} U | \text{HF} \rangle, \\ p_{ij}^{(2)} &= \frac{1}{2} \langle \text{HF} | U^\dagger U^\dagger c_{i\alpha}^\dagger c_{j\alpha} + c_{i\alpha}^\dagger c_{j\alpha} U U | \text{HF} \rangle \\ &\quad + \langle \text{HF} | U^\dagger c_{i\alpha}^\dagger c_{j\alpha} U | \text{HF} \rangle. \end{aligned} \quad (68b)$$

Clearly  $p^{(1)}$  is linear in the correlation coefficients,  $p^{(2)}$  quadratic, and so on. Also, we have

$$\begin{aligned} p_{\gamma\delta}^{(0)} &= \delta_{\gamma\delta}; \quad p_{nm}^{(0)} = 0, \\ p_{ij}^{(1)} &= 0; \quad p_{ij}^{(t)} = 0 \text{ if } t \text{ odd}, \\ p_{ij}^{(2)} &= \langle \text{HF} | U^\dagger c_{i\alpha}^\dagger c_{j\alpha} U | \text{HF} \rangle \\ &= 2^{-1/2} \langle \text{HF} | U^\dagger C_{ij}^\dagger(00) U | \text{HF} \rangle. \end{aligned} \quad (69)$$

With  $U$  of Eq. (32), we have

$$\begin{aligned} [C_{\gamma\delta}^\dagger(00), U] &= -2^{-1/2} \sum_{pq\mu} \sum_S C'_{p\mu, q\gamma}(S) C_{p\mu}^\dagger(S0) C_{q\delta}^\dagger(\bar{S}0), \\ [C_{nm}^\dagger(00), U] &= 2^{-1/2} \sum_{p\mu\nu} \sum_S C'_{p\mu, m\nu}(S) C_{p\mu}^\dagger(S0) C_{n\nu}^\dagger(\bar{S}0). \end{aligned} \quad (70)$$

From Eq. (70) and the results of Appendix C we obtain

$$p_{\gamma\delta}^{(2)} = \delta_{\gamma\delta} \langle \text{HF} | U^\dagger U | \text{HF} \rangle - \frac{1}{2} \sum_{pq\mu} \sum_S C'_{p\mu, q\gamma}(S) C_{p\mu}^*(S) C_{q\delta}^*(S), \quad (71a)$$

$$p_{nm}^{(2)} = \frac{1}{2} \sum_{p\mu\nu} \sum_S C'_{p\mu, m\nu}(S) C_{p\mu}^*(S) C_{n\nu}^*(S), \quad (71b)$$

$$\langle \text{HF} | U^\dagger U | \text{HF} \rangle = \frac{1}{2} \sum_{pq\mu\nu} \sum_S C'_{p\mu, q\nu}(S) C_{p\mu}^*(S) C_{q\nu}^*(S), \quad (72)$$

$$\begin{aligned} \sum_\gamma p_{\gamma\gamma}^{(2)} &= (\frac{1}{2}N - 1) \langle \text{HF} | U^\dagger U | \text{HF} \rangle \\ \sum_m p_{mm}^{(2)} &= \langle \text{HF} | U^\dagger U | \text{HF} \rangle. \end{aligned} \quad (73)$$

Noting that

$$N_0^2 = 1 - \langle \text{HF} | U^\dagger U | \text{HF} \rangle + \dots, \quad (74)$$

we now have

$$p_{\gamma\delta}^{(0)} = \delta_{\gamma\delta}; \quad p_{\gamma\delta}^{(1)} = 0,$$

$$\begin{aligned} \rho_{\gamma\delta}^{(2)} &= p_{\gamma\delta}^{(2)} - \delta_{\gamma\delta} \langle \text{HF} | U^\dagger U | \text{HF} \rangle \\ &= -\frac{1}{2} \sum_{pq\mu} \sum_S C'_{p\mu, q\gamma}(S) C_{p\mu}^*(S) C_{q\delta}^*(S), \end{aligned} \quad (75a)$$

$$\begin{aligned} \rho_{nm}^{(0)} &= p_{nm}^{(1)} = 0, \\ \rho_{nm}^{(2)} &= p_{nm}^{(2)} = \frac{1}{2} \sum_{p\mu\nu} \sum_S C'_{p\mu, m\nu}(S) C_{p\mu}^*(S) C_{n\nu}^*(S), \end{aligned} \quad (75b)$$

$$-\sum_\gamma \rho_{\gamma\gamma}^{(2)} = \sum_m \rho_{mm}^{(2)} = \langle \text{HF} | U^\dagger U | \text{HF} \rangle. \quad (75c)$$

Finally, we have

$$\mathcal{D}_{m\gamma, n\delta} = \mathcal{D}_{m\gamma, n\delta}^{(0)} + \mathcal{D}_{m\gamma, n\delta}^{(1)} + \mathcal{D}_{m\gamma, n\delta}^{(2)} + \dots, \quad (76)$$

$$D_{m\gamma, n\delta} = D_{m\gamma, n\delta}^{(0)} + D_{m\gamma, n\delta}^{(1)} + D_{m\gamma, n\delta}^{(2)} + \dots$$

$$\mathcal{D}_{m\gamma, n\delta}^{(0)} = D_{m\gamma, n\delta}^{(0)} = \delta_{mn} \delta_{\gamma\delta},$$

$$\mathcal{D}_{m\gamma, n\delta}^{(1)} = D_{m\gamma, n\delta}^{(1)} = 0, \quad (77)$$

$$\begin{aligned} \mathcal{D}_{m\gamma, n\delta}^{(2)} &= D_{m\gamma, n\delta}^{(2)} - \delta_{mn} \delta_{\gamma\delta} \langle \text{HF} | U^\dagger U | \text{HF} \rangle \\ &= \delta_{mn} \rho_{\gamma\delta}^{(2)} - \delta_{\gamma\delta} \rho_{mn}^{(2)}. \end{aligned}$$

### VIII. APPROXIMATION TO EQUATIONS OF MOTION

Substitution of Eqs. (46) and (67) into Eq. (14a) gives

$$\begin{bmatrix} \underline{A}(S) & \underline{B}(S) \\ -\underline{B}^*(S) & -\underline{A}^*(S) \end{bmatrix} \begin{bmatrix} \underline{Y}(\lambda S) \\ \underline{Z}(\lambda S) \end{bmatrix} = \omega(\lambda \Gamma S) \begin{bmatrix} \underline{D} & 0 \\ 0 & \underline{D} \end{bmatrix} \begin{bmatrix} \underline{Y}(\lambda S) \\ \underline{Z}(\lambda S) \end{bmatrix}, \quad (78)$$

where the elements of  $\underline{A}$ ,  $\underline{B}$ , and  $\underline{D}$  are defined in Eqs. (47) and (66). There is an equation, Eq. (78), for every irreducible representation  $\Gamma$  of the molecular symmetry group. In addition to Eq. (78) we must also solve

$$\underline{Z}^*(\lambda S) = C(S) \underline{Y}^*(\lambda S). \quad (45)$$

Again there is an equation, Eq. (45), for each irreducible representation  $\Gamma$ .

For the usual RPA we set

$$\underline{A}(S) = \underline{A}^{(0)}(S), \quad \underline{B}(S) = \underline{B}^{(0)}(S), \quad \underline{D} = \underline{D}^{(0)}. \quad (79)$$

The elements of these matrices are shown in Eqs. (53), (60), and (77). In this approximation Eq. (16) becomes

$$\sum_{m\gamma(\Gamma)} [Y_{m\gamma}^{(0)*}(\lambda' S) Y_{m\gamma}^{(0)}(\lambda S) - Z_{m\gamma}^{(0)*}(\lambda' S) Z_{m\gamma}^{(0)}(\lambda S)] = \delta_{\lambda' \lambda}.$$

With the matrices  $\underline{A}^{(0)}(S)$ ,  $\underline{B}^{(0)}(S)$ , and  $\underline{D}^{(0)}$ , Eq. (78) is just the RPA. The RPA has been applied to the atoms<sup>2</sup> Be, Mg, Ca, and Sr, and to the molecules ethylene and formaldehyde.<sup>3</sup>

Thouless<sup>12</sup> has discussed the formal properties of the RPA and shown that all excitation frequencies of the RPA are real provided the HF ground state is stable. The appearance of an imaginary frequency indicates an instability in the HF wave function. In practical calculations, however, the true HF solutions are not available and an excitation frequency may come out imaginary. This can happen even if the HF ground state is well defined. If a

component absent in the practical HF ground state significantly affects the excited states of a certain class, then an instability may occur even if the inclusion of the component in the HF wave function hardly affects the ground-state energy.<sup>13</sup>

For real frequencies in the RPA the solutions  $\underline{Y}^{(0)}$  and  $\underline{Z}^{(0)}$  can be put into Eq. (45) to solve for the correlation coefficients  $\underline{C}$ . If RPA frequencies come out imaginary, we can go to a lower approximation than the RPA and use the Tamm-Dancoff approximation (TDA). The TDA always yields real frequencies. In the usual TDA one keeps only the first term in  $O_\lambda^\dagger$  [Eq. (9)] and takes the HF wave function for the ground-state wave function  $|0\rangle$ . The TDA equations are just

$$\underline{A}^{(0)}(S)\underline{Y}^{(\text{TDA})}(\lambda S) = \omega^{(\text{TDA})}(\lambda\Gamma S)\underline{Y}^{(\text{TDA})}(\lambda S). \quad (80)$$

This assumes that the correlation coefficients are very small. It is still possible to solve Eq. (45) for these coefficients using just the TDA solutions.<sup>11(a)</sup> If these coefficients do not come out small, the calculated values are not reliable. In the RPA the expression for  $\omega$  does not depend on the coefficients  $\underline{C}$ . These correlation coefficients are obtained from Eq. (45) with the  $\underline{Y}^{(0)}$ 's and  $\underline{Z}^{(0)}$ 's of Eq. (78). Hence, the equations cannot be solved self-consistently.

#### Proposed Self-Consistent Scheme: Higher RPA

We now go beyond the RPA. We include terms linear in the correlation coefficients in the elements  $\underline{A}(S)$ ,  $\underline{B}(S)$ , and  $\underline{D}$ :

$$\begin{aligned} \underline{A}(S) &= \underline{A}^{(0)}(S) + \underline{A}^{(1)}(S), \\ \underline{B}(S) &= \underline{B}^{(0)}(S) + \underline{B}^{(1)}(S), \\ \underline{D} &= \underline{D}^{(0)} + \underline{D}^{(1)}. \end{aligned} \quad (81)$$

The elements  $\underline{A}^{(1)}$ ,  $\underline{B}^{(1)}$ , and  $\underline{D}^{(1)}$  are given in Eqs. (56), (64), and (77). Note that

$$\underline{D}^{(1)} = 0, \quad (82)$$

which is a very useful result, since

$$D_{m\gamma, n\delta} = \delta_{mn} \delta_{\gamma\delta} \quad (83)$$

and, hence,

$$\sum_{m\gamma} [Y_{m\gamma}^*(\lambda'S) Y_{m\gamma}(\lambda S) - Z_{m\gamma}^*(\lambda'S) Z_{m\gamma}(\lambda S)] = \delta_{\lambda'\lambda}. \quad (84)$$

With elements  $\underline{A}(S)$ ,  $\underline{B}(S)$ , and  $\underline{D}$  of Eq. (81), Eq. (78) becomes

$$\begin{bmatrix} \underline{A}(S) & \underline{B}(S) \\ -\underline{B}^*(S) & -\underline{A}(S) \end{bmatrix} \begin{bmatrix} \underline{Y}(\lambda S) \\ \underline{Z}(\lambda S) \end{bmatrix} = \omega(\lambda\Gamma S) \begin{bmatrix} \underline{Y}(\lambda S) \\ \underline{Z}(\lambda S) \end{bmatrix}. \quad (85)$$

Clearly these equations are of the same form as those of the usual RPA. But now the elements  $\underline{A}(S)$  and  $\underline{B}(S)$  are functions of the correlation coefficients

$\underline{C}$ 's. We can set up an iterative procedure for solving Eqs. (45) and (85). We take some crude estimates of the  $\underline{C}$ 's, calculate  $\underline{A}^{(1)}(S)$  and  $\underline{B}^{(1)}(S)$  to get  $\underline{A}(S)$  and  $\underline{B}(S)$ , solve Eq. (85), and use those values of  $\underline{Y}$ 's and  $\underline{Z}$ 's in Eq. (45) to obtain new estimates of the  $\underline{C}$ 's. We can iterate these equations for any desired accuracy.

We have applied this scheme to study the low-lying states of the ethylene. Details will be given elsewhere.<sup>7(a)</sup> We obtain vertical excitation energies of 4.95 eV for the  $N \rightarrow T$  transition, 9.4 eV for the  $N \rightarrow V$  transition, and an oscillator strength of 0.47 for the  $N \rightarrow V$ ,<sup>14</sup> while the usual RPA gives 1.50 eV, 7.93 eV, and 0.517, respectively. Experimental values are 4.6 eV, 7.6 eV, and 0.34, respectively.<sup>14</sup>

#### IX. DISCUSSION

Starting from the equations of motion expressed as ground-state expectation values,<sup>6</sup> we have derived a higher-order RPA for excitation frequencies of low-lying states. We represent the ground state as  $e^U|HF\rangle$ , where the operator  $U$  is a linear combination of two-particle-hole operators. The coefficients of this linear combination are just the correlation coefficients and are assumed small. We expand the matrix elements of the equations of motion in a power series of these coefficients and retain up to terms linear in the coefficients  $\underline{C}$ 's. The zero-order approximation is just the RPA. However, the equations with the linear terms added retain the same form as the RPA. These are the equations of the higher RPA. The ground state  $e^U|HF\rangle$  must vanish when acted on by the adjoint of the excited-state creation operator  $O_\lambda^\dagger$ . This condition is expanded in unlinked clusters of particle-hole creation operators giving an equation relating the amplitudes  $\underline{Y}$  and  $\underline{Z}$  of the excited states and the correlation coefficients  $\underline{C}$ 's. This equation and the one determining the excitation frequency are solved self-consistently. This higher RPA removes many deficiencies of the RPA but still ignores second- and higher-order terms. These corrections are certainly small and would be included in a second RPA.<sup>5</sup>

Rowe<sup>6</sup> recently proposed a renormalized RPA in which HF single-particle energies and densities are replaced by renormalized quantities. These renormalized energies can be estimated from experiment and single-particle densities calculated self-consistently. However, certain important terms in the matrix element of  $\underline{B}(S)$  which are linear in the correlation coefficients are neglected in Rowe's renormalized RPA. Also, for applications to molecular spectra we want to calculate the ground-state correlations and excitation frequencies self-consistently. In deriving the RPA in a similar fashion Altick and Glassgold<sup>2</sup> assumed that all terms linear in the correlation coefficients  $\underline{C}$ 's in the expectation value of the operator equations for the excitation frequency



vanished. This is due to the false assumption that in the expectation value of two-particle-hole creation operator over the ground state all terms linear in  $C$  be 0 [see Eq. (19) and statements in the lower half on page 637 of Ref. 2].

We have applied these results to the low-lying  $T$  and  $V$  states of ethylene. The changes in going from the RPA to the higher-order RPA certainly confirms the importance of the first-order corrections which we have included. For example, the predicted excitation energies for low-lying triplets are now in good agreement with experiment. These results will be published separately.<sup>7(a)</sup> We have also developed approximations to the higher RPA and, in fact, show that good solutions to these equations can be obtained using only the potential matrix elements  $V_{ijkl}$  needed in the RPA solution. Solution of the equations requires only a few iterations for self-consistency.

#### APPENDIX A: MULTIPOLE OPERATORS $C_{ij}^\dagger(S, M)$

We define the multipole operators  $C_{ij}^\dagger(S, M)$  as irreducible tensor operators that satisfy the following commutation relations with the spin angular-momentum operator  $\tilde{S}$ :

$$[S_\pm, C_{ij}^\dagger(S, M)] = [S(S+1) - M(M \pm 1)]^{1/2} C_{ij}^\dagger(S, M \pm 1),$$

With Eq. (A4) we obtain the commutator

$$[C_{ij}^\dagger(S, M), C_{i'j'}^\dagger(S', M')] = \sum_{S'' M''} \alpha(S, M; S', M' | S'', M'') [\delta_{ij, i'j'} C_{i'j'}^\dagger(S'', M'') - (-1)^{S+S'+S''} \delta_{ij, i'j'} C_{i'j'}^\dagger(S'', M'')], \quad (A7)$$

where

$$\begin{aligned} \alpha(S, M; S', M' | S'', M'') &= \sum_{\eta=\pm 1/2} (-1)^{1/2-\eta} \langle \frac{1}{2}, M+\eta; \frac{1}{2}, -\eta | S, M \rangle \\ &\quad \times \langle \frac{1}{2}, \eta; \frac{1}{2}, M'-\eta | S', M' \rangle \langle \frac{1}{2}, M+\eta; \frac{1}{2}, M'-\eta | S'', M'' \rangle \\ &= -(-1)^{S''} [2S+1](2S'+1)^{1/2} \langle S, M; S', M' | S'', M'' \rangle \left\{ \begin{matrix} S & S' & S'' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{matrix} \right\}, \end{aligned} \quad (A8)$$

and

$$\left\{ \begin{matrix} S & S' & S'' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{matrix} \right\}$$

is a Wigner 6- $j$  coefficient. A more general expression for  $j$ - $j$  coupling has been given by Dreizler *et al.*<sup>15</sup> In Table I we list the coefficients

$$\sqrt{2} \alpha(S, M; S', M' | S'', M'') = \bar{\alpha}(S, M; S', M' | S'', M'')$$

for various values of  $S, S'$  and  $S''$ .

#### APPENDIX B: MATRIX ELEMENTS OF $\mathcal{D}, \mathcal{G}$ , AND $\mathcal{D}$

Consider the expectation value

$$\begin{aligned} \langle 0 | [C_{ij}(S, M), C_{ki}^\dagger(S', M')] | 0 \rangle \\ = (-1)^M \langle 0 | [C_{ji}^\dagger(S-M), C_{ki}^\dagger(S', M')] | 0 \rangle. \end{aligned} \quad (B1)$$

The commutator transforms under the  $R_3$  group on spin space as the irreducible representations

$$[S_\pm, C_{ij}^\dagger(S, M)] = M C_{ij}^\dagger(S, M). \quad (A1)$$

We also define their Hermitian conjugates as

$$C_{ij}(S, M) = (-1)^M C_{ij}^\dagger(S, -M). \quad (A2)$$

We also introduce the operators  $C_{ij}(\overline{SM})$ , where

$$C_{ij}(\overline{SM}) = (-1)^{S+M} C_{ij}(S, -M). \quad (A3)$$

The subscripts  $i$  and  $j$  refer to spatial orbital states. The operator  $C_{ij}^\dagger(S, M)$  is given by

$$\begin{aligned} C_{ij}^\dagger(S, M) &= \sum_{\eta=\pm 1/2} (-1)^{1/2-\eta} \langle \frac{1}{2}, M+\eta; \frac{1}{2}, -\eta | S, M \rangle \\ &\quad \times c_i^\dagger(M+\eta) c_j(\eta), \end{aligned} \quad (A4)$$

where  $c_i^\dagger(\xi)$  and  $c_i(\xi)$  are the creation and annihilation operators for level  $i$  with spin projection  $\xi = \frac{1}{2}$  or  $-\frac{1}{2}$ . We identify

$$c_i^\dagger(\frac{1}{2}) \equiv c_{i\alpha}^\dagger; \quad c_i^\dagger(-\frac{1}{2}) \equiv c_{i\beta}^\dagger. \quad (A5)$$

These operators satisfy the usual anticommutation relations

$$\{c_i(\xi), c_j^\dagger(\eta)\} = \delta_{ij} \delta_{\xi\eta}, \quad \{c_i^\dagger(\xi), c_j^\dagger(\eta)\} = 0. \quad (A6)$$

The coefficients in Eq. (A4) are just the Clebsch-Gordan coefficients. Equation (10) follows directly from Eq. (A4).

$(S'', M'')$ , where

$$\begin{aligned} S'' &= S+S', \quad S+S'-1, \dots, |S-S'|, \\ M'' &= -M+M'. \end{aligned} \quad (B2)$$

For Eq. (B1) to be nonvanishing the commutator must contain the  $(0, 0)$ -irreducible representation. This is true only for  $S=S'$  and  $M=M'$ . With Eq. (A7) we have

$$\begin{aligned} \langle 0 | [C_{ij}(S, M), C_{ki}^\dagger(S, M)] | 0 \rangle \\ = 2^{-1/2} [\delta_{ik} \langle 0 | C_{ji}^\dagger(00) | 0 \rangle - \delta_{ji} \langle 0 | C_{ki}^\dagger(00) | 0 \rangle], \end{aligned} \quad (B3)$$

which is independent of  $S$  and  $M$ .

By similar arguments we have

$$\begin{aligned} \langle 0 | [C_{ij}(S, M), H, C_{ki}^\dagger(S', M')] | 0 \rangle &= 0, \\ \text{unless } S=S', \quad M=M'. \end{aligned} \quad (B4)$$

The double commutators of Eq. (B4) are independent

TABLE I. The coefficients  $\bar{\alpha}(S, M; S', M' | S'', M'')$ .  
 $\bar{\alpha} = 0$  for all other cases.

$S, M$	$S', M'$	$S'', M''$	$\bar{\alpha}$
1, 1	1, 0	1, 1	-1
	1, -1	$\begin{cases} 1, 0 \\ 0, 0 \end{cases}$	$\begin{cases} -1 \\ -1 \end{cases}$
	0, 0	1, 1	+1
1, 0	1, 1	$\begin{cases} 1, 1 \\ 1, 0 \end{cases}$	$\begin{cases} +1 \\ 0 \end{cases}$
	1, 0	0, 0	+1
	1, -1	1, -1	-1
	0, 0	$\begin{cases} 1, 0 \\ 0, 0 \end{cases}$	$\begin{cases} +1 \\ 0 \end{cases}$
1, -1	1, 1	$\begin{cases} 1, 0 \\ 0, 0 \end{cases}$	$\begin{cases} +1 \\ -1 \end{cases}$
	1, 0	1, -1	+1
	0, 0	1, -1	+1
0, 0	1, 1	1, 1	+1
	1, 0	$\begin{cases} 1, 0 \\ 0, 0 \end{cases}$	$\begin{cases} +1 \\ 0 \end{cases}$
	1, -1	1, -1	+1
	0, 0	$\begin{cases} 1, 0 \\ 0, 0 \end{cases}$	$\begin{cases} 0 \\ +1 \end{cases}$

of  $M$ . This can be shown by examining in the expansion of Eq. (B4). Consider, as an example, the term

$$\begin{aligned} & \langle 0 | C_{ij}(S, M-1) H C_{kl}^\dagger(S, M-1) | 0 \rangle \\ &= [S(S+1) - M(M-1)]^{-1} \\ & \times \langle 0 | C_{ij}(S, M) S_+ H S_- C_{kl}^\dagger(S, M) | 0 \rangle \\ &= \langle 0 | C_{ij}(S, M) H C_{kl}^\dagger(S, M) | 0 \rangle. \end{aligned} \quad (\text{B5})$$

To obtain Eq. (B5) we have used the relations

$$\begin{aligned} & [\tilde{S}^2 - S(S+1)] C_{kl}^\dagger(S, M) | 0 \rangle = 0, \\ & [S_\pm, H] = 0, \quad S_+ S_- = \tilde{S}^2 - S(S+1). \end{aligned}$$

Hence, the matrix elements  $\alpha_{ij,kl}(S)$  and  $\beta_{ij,kl}(S)$  are independent of  $M$ .

#### APPENDIX C: COMMUTATORS OF $C_{m\gamma}^\dagger(S, M)$ AND $U$

We have

$$\begin{aligned} & [C_{m\gamma}(S, M), C_{n\delta}^\dagger(S', M')] = (-1)^M 2^{-1/2} \\ & \times \sum_{S''M''} \bar{\alpha}(S, -M; S', M' | S'', M'') \\ & \times [\delta_{mn} C_{\gamma\delta}^\dagger(S'', M'') - (-1)^{S+S'+S''} \\ & \times \delta_{\gamma\delta} C_{nm}^\dagger(S'', M'')], \\ & [C_{m\gamma}(S, M), C_{n\delta}^\dagger(S', M')] | \text{HF} \rangle = \delta_{S, S'} \delta_{M, M'} \delta_{m\gamma, n\delta} | \text{HF} \rangle. \end{aligned} \quad (\text{C1})$$

The operator  $U$  is

$$U = \frac{1}{2} \sum_{mn\gamma\delta} \sum_S C'_{m\gamma, n\delta}(S) C_{m\gamma}^\dagger(S, 0) C_{n\delta}^\dagger(\bar{S}, \bar{0}), \quad (\text{C3})$$

where

$$C'_{m\gamma, n\delta}(S) = K_{m\gamma, n\delta}(S) + (-1)^S \frac{1}{2} (L_{m\gamma, n\delta} - L_{m\delta, n\gamma}). \quad (\text{C4})$$

Also, we have

$$\begin{aligned} & [C_{m\gamma}(S, M), C_{p\mu}^\dagger(S', 0) C_{q\nu}^\dagger(\bar{S}, \bar{0})] \\ &= C_{p\mu}^\dagger(\bar{S}, \bar{0}) [C_{m\gamma}(S, M), C_{q\nu}^\dagger(S', 0)] \\ &+ C_{q\nu}^\dagger(\bar{S}, \bar{0}) [C_{m\gamma}(S, M), C_{p\mu}^\dagger(S', 0)] \\ &+ (-1)^{S'} [C_{m\gamma}(SM), C_{p\mu}^\dagger(S', 0)], C_{q\nu}^\dagger(S'0)]. \end{aligned} \quad (\text{C5})$$

Thus, we have

$$\begin{aligned} & [C_{m\gamma}(S, M), U] = \sum_{p\mu\nu} \sum_{S'} C'_{p\mu, q\nu}(S') C_{p\mu}^\dagger(\bar{S}', \bar{0}) \\ & \times [C_{m\gamma}(S, M), C_{q\nu}^\dagger(S', 0)] - (-1)^S \\ & \times \sum_{p\mu} \left\{ \begin{matrix} L_{m\mu, p\gamma} & \text{for } M=0 \\ K_{m\mu, p\gamma} & \text{for } M=1 \end{matrix} \right\} C_{p\mu}^\dagger(\bar{S}, \bar{M}), \end{aligned} \quad (\text{C6})$$

$$\begin{aligned} & C_{m\gamma}(S, 0) U | \text{HF} \rangle = \sum_{p\mu} [K_{m\gamma, p\mu} + (-1)^S (L_{m\gamma, p\mu} \\ & - L_{m\mu, p\gamma})] C_{p\mu}^\dagger(\bar{S}, \bar{0}) | \text{HF} \rangle, \\ & C_{m\gamma}(1, \pm 1) U | \text{HF} \rangle = \sum_{p\mu} K_{m\mu, p\gamma} C_{p\mu}^\dagger(\bar{1}, \pm \bar{1}) | \text{HF} \rangle. \end{aligned} \quad (\text{C7})$$

With Eqs. (C2) and (C7), we have

$$\begin{aligned} & \langle \text{HF} | C_{m\gamma}(\bar{S}, \bar{0}) C_{n\delta}(S, 0) U | \text{HF} \rangle = K_{m\gamma, n\delta} \\ & + (-1)^S (L_{m\gamma, n\delta} - L_{m\delta, n\gamma}), \\ & \langle \text{HF} | C_{m\gamma}(\bar{1}, \pm \bar{1}) C_{n\delta}(1, \pm 1) U | \text{HF} \rangle = K_{m\delta, n\gamma}. \end{aligned} \quad (\text{C8})$$

The matrix elements of Eq. (C8) are independent of  $M$ . Hence, for  $S=1$  we have

$$\begin{aligned} & K_{m\gamma, n\delta} - K_{m\delta, n\gamma} = L_{m\gamma, n\delta} - L_{m\delta, n\gamma}, \\ & \langle \text{HF} | C_{m\gamma}(\bar{S}, \bar{M}) C_{n\delta}(S', M') U | \text{HF} \rangle = \delta_{SM, S'M'} C_{m\gamma, n\delta}(S), \end{aligned} \quad (\text{C9})$$

where

$$C_{m\gamma, n\delta} = K_{m\gamma, n\delta} + (-1)^S (K_{m\gamma, n\delta} - K_{m\delta, n\gamma}). \quad (\text{C11})$$

We now have

$$\begin{aligned} & \langle \text{HF} | [U^\dagger, U] | \text{HF} \rangle = \frac{1}{2} \sum_{mn\gamma\delta} \sum_S C_{m\gamma, n\delta}'^*(S) C_{m\gamma, n\delta}(S) \\ & = \sum_{mn\gamma\delta} [K_{m\gamma, n\delta}^2 + \frac{1}{4} (K_{m\gamma, n\delta} - K_{m\delta, n\gamma})^2]. \end{aligned} \quad (\text{C12})$$

Equation (C7) is now written as

$$C_{m\gamma}(SM) U | \text{HF} \rangle = \sum_{p\mu} C_{m\gamma, p\mu}(S) C_{p\mu}^\dagger(\bar{S}, \bar{M}) | \text{HF} \rangle. \quad (\text{C13})$$

#### APPENDIX D: OVERCOUNTING CHARACTERISTIC OF QUASIBOSON APPROXIMATION

Recently Rowe<sup>9</sup> discussed ways to calculate the correlation corrections to the one-body densities needed in the renormalized quasiboson approximation. He pointed out that the corrections to the densities obtained within the quasiboson model are too large by a factor of 2. This point was independently confirmed recently by Johnson, Dreizler, and Klein.<sup>16</sup> Rowe attributed this error in the quasi-

boson model to the fact that the four operators  $C_{m\gamma}^\dagger(SM)C_{n\delta}^\dagger(SM)$  for  $S=0, 1$  in Eq. (34) used in the model are not linearly independent. The purpose of this Appendix is to clarify this.

In our scheme the correlation coefficients  $C(S)$  are evaluated by solving Eq. (45) with given values of  $Y(\lambda S)$  and  $Z(\lambda S)$ . Once this  $C(S)$ 's are evaluated, the coefficients  $K$  are obtained by [see definition of  $C(S)$  [Eq. (38)]]

$$K_{m\gamma, n\delta} = \frac{1}{2} [C_{m\gamma, n\delta}(0) + C_{m\gamma, n\delta}(1)]$$

or

$$K = \frac{1}{2} [\underline{C}(0) + \underline{C}(1)] .$$

Rowe's expressions for the corrections to the one-body densities are explicit functions of  $Z(\lambda S)$ .

The coefficients  $C'(S)$  defined in Eqs. (32) and (33) are obtained by

$$\underline{C}'(0) = \frac{3}{4} \underline{C}(0) + \frac{1}{4} \underline{C}(1) ; \quad \underline{C}'(1) = \frac{1}{4} \underline{C}(0) + \frac{3}{4} \underline{C}(1) .$$

Let us now look at Eq. (34), the quasiboson model expression for  $U$ . We can readily show that this can be also written as

$$U = \frac{1}{2} \sum_{m\gamma n\delta} \sum_{S=0,1} C_{m\gamma, n\delta}''(S) C_{m\gamma}^\dagger(S0) C_{n\delta}^\dagger(\overline{S0}) ,$$

where

$$C_{m\gamma, n\delta}'''(0) = C_{m\gamma, n\delta}''(0) + C_{m\delta, n\gamma}''(1) ,$$

$$C_{m\gamma, n\delta}'''(1) = C_{m\gamma, n\delta}''(1) + C_{m\delta, n\gamma}''(1) .$$

Note that this expression of  $U$  is identical to Eq. (32), the one we used in our scheme, if  $C'''(S)$  are equal to  $C'(S)$ . However, in the quasiboson model, the  $C(S)$  evaluated by Eq. (45) are set equal to  $C''(S)$ , i.e.,

$$\underline{C}''(S) = \underline{C}(S) \text{ (quasiboson approximation).}$$

Thus, we have

$$C_{m\gamma, n\delta}'''(0) = C_{m\gamma, n\delta}''(0) + C_{m\delta, n\gamma}''(1) ,$$

$$C_{m\gamma, n\delta}'''(1) = C_{m\gamma, n\delta}''(1) + C_{m\delta, n\gamma}''(1) .$$

The differences between  $C'(S)$  and  $C'''(S)$  can be more clearly seen in the following expression in terms of  $K$ :

$$C_{m\gamma, n\delta}'(S) = K_{m\gamma, n\delta} + (-)^S \frac{1}{2} (K_{m\gamma, n\delta} - K_{m\delta, n\gamma}) ,$$

$$C_{m\gamma, n\delta}''(S) = 2K_{m\gamma, n\delta} + (-)^S (K_{m\gamma, n\delta} - K_{m\delta, n\gamma}) .$$

Thus, we have

$$\underline{C}'(S) = \frac{1}{2} \underline{C}'''(S) ,$$

which clearly shows that  $C'''(S)$  are twice as large  $C'(S)$ .

The substitution of  $C'''(S)$  into Eqs. (75) for  $C'(S)$  gives us the values of  $\rho_{\gamma\delta}^{(2)}$ ,  $\rho_{mm}^{(2)}$ , and  $\langle \text{HF} | U^\dagger U | \text{HF} \rangle$  which are all twice as large as the correct ones. The correlation wave function of the ground state is  $\approx U | \text{HF} \rangle$ . Thus, the use of  $C'''(S)$  instead of  $C'(S)$  leads to the correlation energy twice as large as the correct one.

It should be, however, noted that these conclusions hold only when these arguments are based on a given set of values of  $Y(\lambda S)$  and  $Z(\lambda S)$ . If the correlation coefficients are to be determined self-consistently, these conclusions will not hold in general. In an iterative scheme like the one we proposed in the present article, the larger magnitudes of the correlation coefficients may produce smaller values after one iteration, and vice versa.

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